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(71) Applicant: CANON KABUSHIKI KAISHA
30-2, Shimomaruko 3-chome
Ohta-ku
Tokyo 146 (JP)

(72) Inventor: YAMADA, Satoru
Canon Kabushiki Kaisha
30-2, Shimomaruko 3-chome
Ohta-ku
Tokyo 146 (JP)
Inventor: MORI, Takahiro
Canon Kabushiki Kaisha
30-2, Shimomaruko 3-chome
Ohta-ku
Tokyo 146 (JP)
Inventor: KATAOKA, Ichiroh
Canon Kabushiki Kaisha
30-2, Shimomaruko 3-chome
Ohta-ku
Tokyo 146 (JP)
Inventor: ITOYAMA, Shigenori
Canon Kabushiki Kaisha
30-2, Shimomaruko 3-chome
Ohta-ku
Tokyo 146 (JP)

(74) Representative: Beresford, Keith Denis Lewis et al
BERESFORD & Co.
2-5 Warwick Court
High Holborn
London WC1R 5DJ (GB)

(54) **SOLAR CELL MODULE HAVING SURFACE COATING MATERIAL OF THREE-LAYER STRUCTURE.**

(57) A solar cell module of the type wherein a photovoltaic device (solar cell) is covered with a packing material, and its light-receiving side is covered with a three-layer structure. The three-layer structure comprises a rigid resin layer having a Shore hardness D of at least 50; an adhesive layer that absorbs UV rays of wavelenghts capable of deteriorating the rigid resin layer but transmits UV rays necessary for power generation by the photvoltaic device, and an outermost layer having high weatherability (the property that the resin itself is stable against heat, light and moisture).

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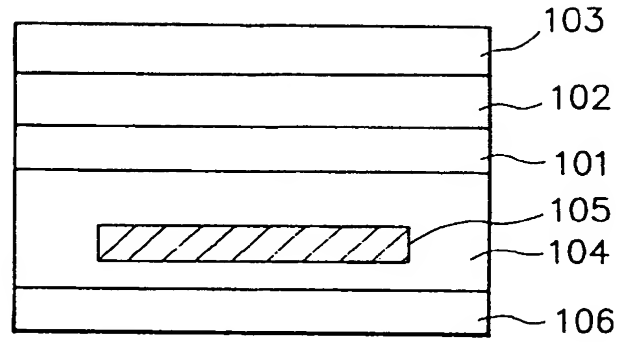
FIG. 1



BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a solar cell module which excels in weatherability, heat resistance, moisture resistance and scratch resistance and which has an excellent protective ability against an external pressure. More particularly, the present invention relates to a solar cell module comprising a photovoltaic element (that is, a solar cell) enclosed by a filler material and a coating material having a three-layered structure which is disposed on a light receiving surface of the solar cell, wherein said coating material is composed of a layer made of hard resin having a hardness of 50 or more in Shore hardness D (hereinafter, referred to as a hard resin layer); a layer having a function of absorbing ultraviolet rays liable to deteriorate the hard resin layer and of transmitting light necessary for photoelectric conversion of the solar cell and also having an adhesive function (hereinafter, referred to as an adhesive layer); and a layer made of a resin excellent in weatherability (the resin itself being stable against heat, light and moisture) (hereinafter, referred to as an outermost layer), said hard resin layer, adhesive layer and outermost layer being laminated on the light receiving surface side of the photovoltaic element in this order from the light receiving surface side. The coating material having the above-described three-layered structure in the solar cell module of the present invention prevents the photovoltaic element from being applied with an external pressure, and satisfies the weatherability, heat resistance, moisture resistance and scratch resistance necessary for the solar cell module.

Related Background Art

Conventionally, a number of thin film solar cells have been proposed. The typical one of the thin film solar cells is an amorphous silicon thin film solar cell (a-Si thin film solar cell). As for the a-Si thin film solar cell, there has been known a type in which an a-Si semiconductor film functioning as a photoelectric conversion element is provided on a conductor substrate and a transparent conductive layer is provided on the semiconductor thin film. In the case where the a-Si thin film solar cell having the above construction is used as a power supply means, the surface of the a-Si solar cell on the light incident side must be protected, unlike a solar cell having a construction using a glass board as the substrate. For this purpose, a protective means is provided on the surface of the a-Si solar cell on the light incident side. In this protective means, it is most important to sufficiently transmit sunlight and hence to keep the conversion efficiency of the solar cell. The protective means is also required to have an ability of protecting the interior of the solar cell against wind and rain and the other external pressure (hereinafter, referred to as an interior protective ability). It is also important for the protective means itself to be prevented from being deteriorated, colored and reduced in mechanical strength due to light, heat and moisture. As such a protective means, there has been known a type in which a transparent resin layer excellent in weatherability is provided on the light receiving surface side as a surface coating layer, and a filler material made of thermoplastic transparent resin is provided inside the transparent resin layer. The resin layer as the surface coating layer is generally composed of an acrylic resin film or a fluororesin film such as a tetrafluoroethylene-ethylene copolymer film or polyvinyl fluoride film. As described above, the above filler material is interposed between the surface coating layer and the solar cell. As the filler material, there is generally used EVA (ethylene-vinyl acetate copolymer), butyral resin or the like. A back surface film is provided on the back surface of the conductive substrate of the solar cell by way of a filler material. As the back surface film, there is used a nylon film, a fluororesin laminated aluminum film or the like. Moreover, in the practical solar cell module, a reinforcing material is provided on the back surface of the above back surface film by way of a filler material. Hence, each of the filler materials interposed between the surface coating layer and the solar cell and between the conductive substrate and the back surface film is required to have a function as an adhesive and a function of protecting a photovoltaic element from scratch damage and impact applied from the exterior.

The interior protective ability of the protective means having the above construction, however, is dependent on the thickness of the coating material composed of the surface coating layer on the light receiving surface and the filler material. Specifically, as the thickness of the coating material is increased, the interior protective ability is increased; and as it is decreased, the interior protective ability is reduced. However, when the thickness of the surface coating layer on the light receiving surface side is increased, separation tends to be generated at the interface between the surface coating layer and the filler material due to temperature change. The separation thus generated causes a problem in that moisture reaches a solar cell through the separated portion, and thereby not only the characteristics of the solar cell are reduced but also a leak current is generated by way of the permeating moisture. The filler material which

encloses the solar cell is required to have a function of filling the irregularities of the solar cell therewith and of being stuck on the surface coating layer. The filler material is thus required to have a rubber elasticity. Moreover, as the thickness of the surface coating material is increased, the light transmissivity thereof is reduced, to thus lower the conversion efficiency of the solar cell. The solar cell module having the above construction is generally manufactured in the following procedure. Namely, a resin film as the surface coating layer on the light receiving surface side, a surface side filler material, a solar cell, a back surface side filler material, and a back surface film are laminated, and are then hot-pressed using a vacuum laminater. In this manufacturing method, since the end portion of the solar cell module comes to be in a close-contact state upon hot-pressing, air sometimes remains in part of the interior between the filler material and the surface coating material on the light receiving surface side and between the filler material and the solar cell. As a result, bubbles often remain in the sealed solar cell module. The bubbles thus remaining in the solar cell module is repeatedly expanded and contracted due to temperature change, thus leading to the separation of the coating material. The separation thus generated causes the above-described problem that moisture reaches the solar cell through the separated portion and thereby the conversion efficiency is reduced. Moreover, the remaining bubbles deteriorate the appearance of the solar cell module, thereby reducing the yield of products.

As a means for solving the above-described problem, there has been known a method of inserting glass fiber unwoven fabric between the filler material and the surface coating layer on the light receiving surface side and between the filler material and the solar cell, and then laminating them. In this method, the surface coating material is reinforced by glass fibers, and it is thus improved in its mechanical strength. The interior protective ability of the surface coating material against an external force is increased because of the increased mechanical strength, and thereby the thickness of the surface coating material can be relatively thinned. This makes it possible to prevent the above separation easier to be generated when the thickness of the surface coating layer on the light receiving surface side is large. Moreover, since the thickness of the surface coating material can be relatively thinned, it becomes possible to suppress the reduction in the light transmissivity of the surface coating material and hence to prevent the reduction in the conversion efficiency of the solar cell. In the manufacturing process of the solar cell module, since glass fibers are interposed between the filler material and the solar cell and between the solar cell and the surface coating layer on the light receiving surface side, even when the solar cell module is pressed, air vent passages can be ensured at the end portion of the solar cell module, thereby making easy the evacuation and eliminating the remaining bubbles. In this case, however, the glass fibers are inevitably exposed from the end portion of the solar cell module, and thereby moisture easily permeates in the solar cell module by way of the glass fibers, and the permeating moisture sometimes exerts adverse effect on the solar cell. To prevent the glass fibers from being exposed from the end portion of the solar cell module, there may be considered a method of previously cutting the glass fibers in a size smaller than that of the solar cell module; however, in this case, the end portion of the solar cell module is lack in air vent passages similarly to the structure with no glass fibers, thereby generating the remaining bubbles. This method, therefore, fails to sufficiently solve the above-described problem.

SUMMARY OF THE INVENTION

The present inventors have earnestly studied to solve the above-described problems of the prior art solar cell modules, and have accomplished the present invention.

Namely, the present inventors have experimentally examined the problems of the above-described coating materials of the prior art solar cell modules, and found a knowledge that the above-described problems of the prior art solar cell module can be solved without glass fibers used in the prior art by a method wherein a photovoltaic element (solar cell) is enclosed by a filler material and a surface coating material having a multi-layer structure containing a hard resin layer is disposed on the light receiving surface side of the photovoltaic element.

On the basis of the above-described knowledge, the present invention has been accomplished.

A principal object of the present invention is to provide an improved solar cell module having a surface coating material satisfying characteristics required for the solar cell module without glass fibers used in the prior art, thereby solving the above-described problems of the prior art solar cell modules.

Another object of the present invention is to provide a solar cell module having a surface coating material which excels in weatherability, heat resistance, and adhesiveness with a photovoltaic element (solar cell), and which has a function of protecting the photovoltaic element (solar cell) from a force applied from the exterior (external pressure) and of suppressing the deterioration of the photovoltaic element (solar cell) due to moisture permeation at minimum, thereby achieving a desired conversion efficiency for a long period

of time.

A further object of the present invention is to provide an improved solar cell module comprising a photovoltaic element (solar cell) enclosed by a filler material and a coating material having a three-layered structure disposed on the light receiving surface side of the photovoltaic element, wherein said coating element includes a hard resin layer having a hardness of 50 or more in Shore hardness D; an adhesive layer having a function of absorbing ultraviolet rays with such a wavelength to deteriorate the hard resin layer and of transmitting ultraviolet rays necessary for power generation of the photovoltaic element, and also having a layer adhesive function; and an outermost layer excellent in weatherability (the resin itself being excellent in a stability against heat, light and moisture), said hard resin layer, adhesive layer and outermost layer being laminated in this order, whereby even when an external force (external pressure) is applied, the photovoltaic element is stabilized and the surface coating material is excellent in weatherability, heat resistance and moisture resistance, without generation of any separation; and the photovoltaic element is prevented from being deteriorated even upon use in outdoors for a long period of time, thus achieving a desired photoelectric conversion efficiency.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic cross-sectional view of one example of a solar cell module of the present invention;

FIG. 2 is a schematic cross-sectional view of one example of a solar cell element used for the solar cell module shown in FIG. 1;

FIG. 3 is a schematic illustrative view of scratch test;

FIG. 4 is a view showing component members of one example of a solar cell module of the present invention;

FIG. 5 is a view showing component members of a prior art solar cell module; and

FIG. 6 is a view showing component members of another example of a prior art solar cell module.

DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

The present invention is to solve the above-described problems in the prior art solar cell modules and to achieve the above-described objects. A solar cell module of the present invention has the following construction. Namely, the solar cell module comprises a photovoltaic element (solar cell) enclosed by a filler material and a coating material having a three-layered structure disposed on the light receiving surface side of the photovoltaic element, wherein said coating element includes a hard resin layer having a hardness of 50 or more in Shore hardness D; an adhesive layer having a function of absorbing ultraviolet rays with such a wavelength to deteriorate the hard resin layer and of transmitting ultraviolet rays necessary for power generation of the photovoltaic element, and also having a layer adhesive function; and an outermost layer excellent in weatherability (the resin itself being excellent in a stability against heat, light and moisture), said hard resin layer, adhesive layer and outermost layer being laminated in this order. The coating material having the above-described three-layered structure in the solar cell module of the present invention includes the following functions: (1) to prevent the photovoltaic element from being applied with an external pressure and hence to protect the solar cell; (2) to satisfy weatherability, heat resistance, moisture resistance and scratch resistance necessary for the solar cell module; (3) to ensure the adhesiveness with the photovoltaic element (solar cell); (4) to suppress the deterioration of the photovoltaic element (solar cell) due to moisture permeation at minimum; and (5) to achieve a desired conversion efficiency of the photovoltaic element for a long period of time.

Hereinafter, the solar cell module having the above construction according to the present invention will be described in detail.

FIG. 1 is a schematic cross-sectional view of a solar cell module of the present invention. In FIG. 1, reference numeral 101 indicates a hard resin layer; 102 is an adhesive layer; 103 is an outermost layer; 104 is a filler material layer; 105 is a photovoltaic element; and 106 is a back surface insulating layer. In the solar cell module shown in FIG. 1, sunlight is impinged through the outermost layer 103, passing through the adhesive layer 102, hard resin layer 101 and filler material layer 104, and reaches the photovoltaic element 105. Thus, an electromotive force is generated by the photovoltaic element 105.

Each component of the solar cell module of the present invention will be described below.

Hard Resin Layer

The hard resin layer 101 is made of a resin having a hardness of 50 or more in Shore hardness D. The hard resin layer 101 is required to be excellent in transparency and to exhibit a strong resistance against an external pressure and the like. The hard resin layer is made of high density polyethylene (60 or more in Shore hardness D), polycarbonate (70 or more in Shore hardness D), polyethylene terephthalate being a polyester resin (80 or more in Shore hardness D), polyarylate (70 or more in Shore hardness D) or polyamide resin (70 or more in Shore hardness D). Specific example of these resins preferably include polycarbonate, polyethylene terephthalate as a polyester resin, and polyarylate. Each of these resins is preferably used in the form of a film. Of these resins, the polycarbonate film is very high in mechanical strength, and it is poor in weatherability but is difficult to be reduced in coloring and in mechanical strength by shielding of ultraviolet rays by the adhesive layer, with a result that it is sufficient to be practically used. In the case of polyethylene terephthalate, the biaxial orientated film thereof is preferable because it is very high in mechanical strength and is not torn and pierced by a pressure applied from the exterior. The polyarylate resin film has a very high heat resisting temperature and thereby it sufficiently withstands the operation at a high temperature. To keep the mechanical strength without reduction in transmissivity, the thickness of the hard resin layer 101 is preferably in the range of from 25 to 200 μm, more preferably, in the range of from 75 to 125 μm.

Incidentally, in the hard resin films used for the prior art solar cell modules, there is known a type containing an ultraviolet absorbent for improving the weatherability. However, the layer formed of such a hard film absorbs light having a wavelength less than about 400 nm, thus reducing the conversion efficiency of the photovoltaic element. In the present invention, therefore, such a hard film is not used.

The above-described hard resin film used as the hard resin layer 101 is preferably subjected to corona discharge treatment, ozonation or primer coating treatment for ensuring the adhesiveness with the filler material 104 and the adhesive layer 102.

Adhesive Layer

The adhesive layer 102 is required to exhibit a function of protecting the hard resin layer 101 from ultraviolet rays and of sufficiently transmitting light necessary for photoelectric conversion of the photovoltaic element. Moreover, it must ensure the adhesive strength with the outermost layer 103 and the hard resin layer 101. In the case where the photovoltaic element is made of a-Si and has a plurality of photoelectric conversion layers, the wavelengths of light photoelectrically converted in respective photoelectric conversion layers are different from each other. If light necessary for a layer which converts light having a short-wavelength into a power is shielded by the adhesive layer 102, a current generated in the photoelectric conversion layer is reduced, thus lowering the conversion efficiency of the photovoltaic element. To prevent the reduction in the conversion efficiency of the photovoltaic element, the adhesive layer 102 is made of a specified resin film having a total light transmissivity which is preferably 90% or more for light having a wavelength of 400 nm or more, 50% or more for 380 nm, and 10% or less for 350 nm or less; more preferably, 95% or more for 400 nm or more, 80% or more for 380 nm, and less than 5% for 350 nm or less. To realize the total light transmissivity of the adhesive layer, the adhesive layer is formed of a resin having the following adhesiveness which is mixed with the following ultraviolet absorbent in a specified amount. Moreover, the adhesive layer 102 is required to be transparent against light used for photoelectric conversion. Specific examples of the resins which satisfy the requirements for the adhesive layer and which can form a desired adhesive layer, include ethylene-vinyl acetate copolymer (EVA), polyvinyl butyral (PVB), silicon resin, and acrylic resin. In the case where the adhesive strength of the adhesive layer 102 is insufficient, the adhesive strength can be enhanced using silane coupling agent or titanate coupling agent. The above adhesive resin constituting the adhesive layer 102 is preferably added with an ultraviolet absorbent for giving a desired ultraviolet ray shielding function to the adhesive layer. The ultraviolet absorbents used include an organic ultraviolet absorbent, and inorganic ultraviolet absorbent. As the organic ultraviolet absorbent, there may be preferably used a benzophenyl series, salicylate series, benzotriazole series and acrylonitrile series ultraviolet absorbent. More preferably, specific examples of the organic ultraviolet absorbents include 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-n-octoxybenzophenone, and 2-(2-hydroxy-5-t-octylphenyl)-benzotriazole. Specific examples of the inorganic ultraviolet absorbents preferably include TiO_2, CeO_2, ZnO and SnO_2.

Outermost Layer

It is important that the outermost layer 103 is stable against heat, light and moisture (excellent in weatherability). Moreover, the outermost layer is desirable to prevent the reduction in the efficiency of the photovoltaic element due to contamination. For this purpose, the outermost layer is desirable to be excellent in water repellency. The water repellency is preferably 50° or more, more preferably, 70° or more in terms of contact angle with water. The outermost layer 103 is formed of fluororesin or silicon resin. In the preferred mode, the outermost layer 103 is formed of fluororesin. Specific examples of the fluororesins include tetrafluoroethylene-ethylene copolymer, trifluoroethylene chloride resin, tetrafluoroethylene-perfluoroalkyl vinylether copolymer, tetrafluoroethylene-hexafluoropropylene, fluorovinylidene, and fluorovinyl resin. The outermost layer made of such resins is preferably subjected to corona treatment, ozonation or primer coating for ensuring the adhesive strength with the adhesive layer 102.

Filler Material Layer

The filler material layer 104 is required to have an adhesive strength between the back surface insulating film 101 and the photovoltaic element 105, and between the photovoltaic element 105 and the hard resin layer 101. The filler material layer is essential to be thermoplastic for filling the irregularities on the photovoltaic element 105 and giving smoothness to the hard resin layer. The filler material layer positioned on the light incident side of the photovoltaic element 105 is required to be transparent. The filler material layer 104 is made of ethylene-vinyl acetate copolymer (EVA), polyvinyl buthyral (PVB), silicon resin, epoxy resin or acrylic resin. The filler material layer positioned on the back surface may be opaque. The resin used for the filler material layer can be added with a crosslinking agent, thermal oxidation preventive agent and the like for improving the heat resistance, and also may be added with an ultraviolet absorbent or light oxidation preventive agent for improving the light stability. In the case where the adhesive strength between the filler material layer and the photovoltaic element is insufficient, the adhesive strength can be improved by the addition of a silane coupling agent or titanate coupling agent.

Photovoltaic Element (Solar Cell)

The photovoltaic element 103 of the present invention is so constructed that a semiconductor photoactive layer as a photoelectric conversion member is formed at least on a conductive substrate. FIG. 2 is a schematic view showing the construction of one example of the photovoltaic element. In FIG. 2, reference numeral 201 indicates a conductive substrate, 202 is a back surface reflection layer, 203 is a semiconductor photoactive layer, 204 is a transparent conductive layer, and 205 is a collecting electrode. The conductive substrate 201 functions as a base of the photovoltaic element (solar cell), and also serves as a lower electrode. The conductive substrate 201 is composed of silicon, tantalum, molybdenum, tungsten, stainless steel, aluminum, copper, titanium, carbon sheet, lead plating steel plate, resin film formed with a conductive layer or ceramics. On the conductive substrate 201, a metal layer, metal oxide layer, or metal layer and metal oxide layer may be formed as the back surface reflection layer 202. In this case, the metal layer can be made of, for example, Ti, Cr, Mo, W, Al, Ag, or Ni. The metal oxide layer is made of, for example, ZnO, TiO_2 or SnO_2. The metal layer and the metal oxide layer can be formed by resistance heating evaporation, electron beam evaporation or sputtering. The semiconductor photoactive layer 203 is used for photoelectric conversion, and it is made of a pn-junction polycrystalline silicon, pin-junction amorphous silicon, or a compound semiconductor such as $CuInSe_2$, $CuInS_2$, GaAs, Cds/Cu_2S, CdS/CdTe, CdS/InP or $CdTe/Cu_2Te$. The semiconductor photoactive layer, which is composed of polycrystalline silicon, can be formed by a method in which molten silicon is molded into a sheet or amorphous silicon is heat-treated. The semiconductor photoactive layer, which is composed of amorphous silicon, is formed by plasma CVD using silane gas as a raw material. The semiconductor photoactive layer, which is composed of a compound semiconductor, is formed by ion plating, ion beam deposition, vacuum evaporation, sputtering, or electrodeposition. The transparent conductive layer 204 serves as an upper electrode of the photovoltaic element (solar cell). The transparent conductive layer 204 is made of, for example, In_2O_3, SnO_2, In_2O_3-SnO_3-SnO_2 (ITO), ZnO, TiO_2, Cd_2SnO_4 or a crystalline semiconductor layer highly doped with impurities. The transparent conductive layer 204 can be formed by resistance heating evaporation, sputtering, spraying, CVD or impurity diffusion. A grid-like collecting electrode 205 (grid) may be provided on the transparent conductive layer 204 for effectively collecting a current. As a specific example of the material used for the collecting electrode 205, there is used a conductive paste in which fine-powder of silver, gold, copper, nickel or carbon is diffused in a binder polymer. Specific examples of

the binder polymers include resins such as polyester, epoxy, acryl, alkyd, polyvinyl acetate, rubber, urethane, and phenol. In the case of using the above conductive paste, the collecting electrode is formed by a coating method. Other than this method, the collecting electrode can be formed by sputtering using a mask pattern, resistance heating, CVD, a patterning method in which a metal film is evaporated over the whole surface and unnecessary portions are removed by etching, a method of directly forming a grid electrode pattern by photo-CDV, and a method of forming a mask of a negative pattern of a grid electrode pattern followed by plating. Output terminals 206 are mounted to the conductive substrate and the collecting electrode for taking out an electromotive force. The output terminal is mounted on the conductive substrate by a method wherein a metal body such as a copper tab is joined by spot welding or soldering. The output terminal is mounted on the collecting electrode by a method wherein the metal body is electrically connected using conductive adhesive or a solder 207. In mounting the output terminal to the collecting electrode 205, an insulator 208 is preferably provided for preventing short-circuit due to contact between the output terminal and the conductive substrate and semiconductor layer. The photovoltaic element (solar cell) having the above construction is connected in series or in parallel in accordance with a desired voltage or current. A plurality of the photovoltaic elements having the above construction can be integrated on an insulated substrate to obtain a desired voltage or current.

Back Surface Insulating Layer

In the case of a photovoltaic element (solar cell) having a conductive substrate, the back surface insulating layer 106 is provided to perfectly insulate the conductive substrate from the outside of the solar cell module. The back surface insulating layer 106 is formed of a film of nylon, polyethylene, polyester or polystyrene.

Hereinafter, the present invention will be described in detail with reference to examples. In addition, the present invention is not limited to the examples.

Example 1

In this example, a solar cell module having a construction shown in FIG. 1 was prepared.

First, there were prepared a back surface insulating layer member 401, a back surface side filler material member 402, a photovoltaic element (solar cell) 403, a front surface side filler material member 404, a hard resin layer member 405, an adhesive layer member 406, and an outermost layer member 407. These members 401 to 407 were then laminated as shown in FIG. 4, to prepare the solar cell module of the present invention.

As the back surface insulating layer member 401, nylon (trademark name: DARTEK (thickness: 75 μm), produced by Du Pont Company) was used.

Each of the filler material layer members 402 and 404, and the adhesive layer member 406 was prepared as follows: Namely, 100 parts by weight of EVA (trademark name: EVAFLEX 150, produced by Mitsui/Du Pont Poly Chemical Company), 1.5 parts by weight of a crosslinking agent (trademark name: LUPERSOL, produced by Penwort Company), 0.3 parts by weight of a UV absorbent (trademark name: Cyasorb 531, produced by Cyanamid Company), 0.2 parts by weight of an oxidation preventive agent (trademark name: Nowguard P, produced by Uniroyal Company), and 0.1 parts by weight of a light stabilizer (trademark name; Chinubin 770, produced by Chibaguigy Company) were mixed, and the resultant mixture was extruded by an extruder having a T die, to prepare each member in the form of a film. The thickness of the film as the adhesive layer member 406 thus prepared was 100 μm. The thickness of the film as each of the filler material layer members 402 and 406 was 150 μm.

The photovoltaic element 403 having the construction shown in FIG. 2 was prepared as follows: Namely, a strip-like stainless steel substrate 201 previously cleaned was first prepared. On the substrate, an Al layer (thickness: 5000 Å) and a ZnO layer (thickness: 5000 Å) were sequentially formed as the back surface reflection layer 202 by sputtering. Then, a tandem type a-Si photoelectric conversion semiconductor layer 203 having a structure of an n-layer (film thickness 150 Å)/i-layer (film thickness 4000 Å)/p-layer (film thickness 100 Å)/n-layer (film thickness 100 Å)/i-layer (film thickness 800 Å)/p-layer (film thickness 100 Å) was prepared by plasma-CVD. In this case, the n-type a-Si layer was formed using a mixed gas of SiH_4, PH_3 and H_2; the i-type a-Si layer was formed using a mixed gas of SiH_4 and H_2, and the p-type fine crystal μc-Si layer was formed using a mixed gas of SiH_4, BF_3 and H_2. Next, an In_2O_3 thin film (thickness: 700 Å) as the transparent conductive layer 204 was formed by a method wherein In was evaporated under an O_2 atmosphere by resistance heating. The sample thus obtained was cut in a plurality of elements (size: 30 cm × 15 cm). Of a plurality of the elements, two pieces were selected, each of which was formed with a

collecting grid electrode 205 by screen printing using silver paste (trademark number: #5007, produced by Du Pont Company), to thus obtain a solar cell element. Two pieces of the solar cell elements were connected in series to each other by bonding using silver paste (trademark number: #220, produced by Kesuru Company) by way of a copper tab (thickness: 50 μm). Moreover, an output terminal from the stainless steel substrate was mounted using a copper tab (thickness: 50 μm) and silver paste (trademark number: #220 produced Kesuru Company). Next, a polyamide resin (trademark name: Kapton film (thickness: 50 μm), produced by 3M Company) was provided on the element as the insulator 208 as shown in FIG. 2, and another output terminal was connected using a copper tab (thickness: 50 μm) and silver paste (trademark number: #220, produced by Kesuru Company). Thus, the photovoltaic element 403 was prepared.

As the hard resin layer member 405, a polycarbonate film (trademark name: IUPILON (thickness: 100 μm, hardness: 82 in Shore hardness D), produced by Mitsubishi Gas Chemical Company) was prepared. The bonding surface of the polycarbonate film with the filler material and the adhesive layer was subjected to corona discharge treatment.

As the outermost resin member 407, an ETFE as a fluororesin film (trademark name: AFLEX (thickness: 50 μm), produced by Asahi Glass Company) was prepared. The bonding surface of the ETFE film with the adhesive layer was subjected to corona treatment.

On an aluminum plate (thickness: 20 mm) having a heat source, the back surface insulating layer member 401, back surface side filler material layer member 402, photovoltaic element 403, front surface side filler material member 404, hard resin layer member 405, adhesive layer member 406 and outermost member 407 were laminated in this order, to obtain a laminated body. A sheet made of heat resisting silicon rubber (thickness: 3 mm) was placed on the laminated body. Subsequently, the interior of the laminated body was evacuated in a vacuum of 10 mmHg by a vacuum pump. In this case, an O-ring was used as a sealant. After being sufficiently evacuated, the laminated body was heated from room temperature to 150 °C and held at 150 °C for 20 min. Thus, a solar cell module was obtained. In this way, a plurality of the solar cell module was obtained.

The solar cell modules thus obtained ware evaluated in the following procedure.

Scratch Test

This test was made to examine whether the protective ability of the surface coating material of the solar cell module against the scratch applied from the exterior is sufficient or not. In this test, a steel made blade 302 was first moved along the surface of the solar cell module in the direction of the arrow D at a speed of 152.4 mm/sec while a load (F) of 4 lbs was applied. The evaluation in this test was made by a method wherein a high voltage dielectric breakdown test was performed in the following manner after the scratch test, and the standard was determined such that the solar cell module in which the generated leak current was less than 50 μA was acceptable. The scratch test was performed on the upper and outer surface of the tab as the connection member located at the highest position in the solar cell module. The high voltage dielectric breakdown test will be described below. The anode and cathode of the solar cell module after the scratch test were short-circuited. The sample thus obtained was dipped in a solution having an electric conductivity of 3500 ohm • cm (containing 0.1 wt% of Triton X-100 (trademark name) as a surface active agent in an amount of 0.1 wt%. At this time, the scratched portion was dipped while the output terminal of the sample was not dipped in the solution. The cathode of a power source was dipped in the solution and the anode of the power source was connected to the output terminal of the sample. The evaluation was performed in the condition that a voltage of 2000 V was applied. The evaluated results are shown in Table 1 in accordance with the following standard: namely, a mark O indicates the case where only a current less than 0.5 μA is allowed to flow, and a mark X indicates the case where a current of 0.5 μA or more is allowed to flow.

Hail Impact Test

This test is performed to examine the presence or absence of the protective ability of the interior of a solar cell module against an external pressure. This test was performed in the following procedure: Namely, ten pieces of ice balls each having a diameter of one inch are made to collide with each portion of a solar cell module in which the mechanical strength is weak (the center of the photovoltaic element, corners of the module, edges, connection portion of the photovoltaic element) at a speed of 23.2 m/sec. The solar cell module thus tested was evaluated in terms of the presence or absence of separation and cracking, and in terms of photoelectric conversion efficiency. The evaluation for the presence or absence of separation and

cracking was visually performed. The evaluation for the photoelectric conversion efficiency was performed by a method wherein the photoelectric conversion efficiencies before and after the Hail impact test were measured, and a change ratio therebetween was examined. The evaluated results are shown in Table 1 in accordance with the following standard; namely, a mark ◎ indicates the case where separation and cracking are not observed at all, and the change ratio is less than 5%, a mark O indicates the case where separation and cracking are slightly observed but the change ratio is less than 5%, and a mark X indicates the case where separation and cracking are frequently observed and the change ratio is 5% or more.

Adhesive Force in High Temperature/High Moisture

A solar cell module was reserved for 100 hours in the condition of 85°C/85% (relative moisture), and the adhesive strength of the solar cell module at the end portion of the coating material was qualitatively evaluated in the condition of 85°C/85% (relative moisture) by a crossing-type separation method. The evaluated results are shown in Table 1 in accordance with the following standard: namely, a mark ◎ indicates the case where the adhesive strength is excellent, a mark O indicates the case where the adhesive strength is sufficient to be practically used, and a mark X indicates the case where the adhesive strength is insufficient.

Weatherability

A solar cell module was subjected to an accelerating weatherability test. Specifically, the solar cell module was put in a sunshine weather meter and was subjected to light emission and rain drop cycle for 5000 hours, after which it was evaluated in terms of the appearance change and photoelectric conversion efficiency. The appearance change was visually evaluated, and the evaluated results are shown in Table 1 in accordance with the following standard: namely, a mark ◎ indicates the case where the appearance change is not observed at all, a mark O indicates the case where the appearance change is slightly observed but is sufficient to be practically used, and a mark X indicates the case where the appearance is insufficient to be practically used because separation, cracking and coloring are observed.

The photoelectric conversion efficiency was evaluated by a method wherein the photoelectric conversion efficiency of the solar cell module after testing was measured, and the measured value was compared with the photoelectric conversion efficiency before testing (this was taken as 1), to obtain a relative value. Accordingly, the value shown in Table 1 is the relative value. In addition, the deterioration of the photovoltaic element itself of amorphous silicon was omitted.

Durability against Temperature Change

The solar cell module was subjected to a testing cycle (-40°C/one hour: 85°C/one hour) by 50 times, and the appearance of the solar cell module was visually evaluated. The evaluated results are shown in Table 1 in accordance with the following standard: namely, a mark ◎ indicates the case where the appearance change is not observed at all, a mark O indicates the case where the appearance change is slightly observed but is sufficient to be practically used, and a mark X indicates the case where the appearance is insufficient because separation, cracking and coloring are observed to the extent largely obstructing reliability.

Example 2

A plurality of solar cell modules were obtained in the same procedure as in Example 1, except that the resin used for the hard resin layer member 405 was replaced with a polyethylene terephthalate film (trademark name: LUMIRROR (thickness: 50 μm, hardness: 90 in Shore hardness D), produced by TORAY INDUSTRIES).

The solar cell modules thus obtained were evaluated in the same procedure as in Example 1. The evaluated results are shown in Table 1.

Example 3

A plurality of solar cell modules were obtained in the same procedure as in Example 1, except that the resin used for the hard resin layer member 405 was replaced with a polyarylate film (trademark name: EMBLATE (thickness: 100 μm, hardness: 77 in Shore hardness D), produced by UNITIRA).

The solar cell modules thus obtained were evaluated in the same procedure as in Example 1. The evaluated results are shown in Table 1.

Example 4

A plurality of solar cell modules were obtained in the same procedure as in Example 1, except that the resin used for the adhesive layer member 406 was replaced with a butyral resin.

The solar cell modules thus obtained were evaluated in the same procedure as in Example 1. The evaluated results are shown in Table 1.

Example 5

A plurality of solar cell modules were obtained in the same procedure as in Example 1, except that the resin used for the adhesive layer member 406 was replaced with methylbutyl methacrylate copolymer.

The solar cell modules thus obtained were evaluated in the same procedure as in Example 1. The evaluated results are shown in Table 1.

Comparative Example 1

First, there were prepared a back surface insulating layer member 501, a back surface side filler material member 502, a photovoltaic element (solar cell) 503, a front surface side filler material member 504 and an outermost layer member 505. These members were then laminated as shown in FIG. 5 in the same procedure as in Example 1.

The back surface insulating layer member 501, back surface side filler material member 502, photovoltaic element (solar cell) 503, and outermost layer member 505 were made to be the same as those in Example 1. The front surface side filler material member 504 was prepared in the same procedure as in Example 1, except that the thickness was changed to 350 µm. Thus, a plurality of solar cells were obtained.

The solar cell modules thus obtained were evaluated in the same procedure in Example 1. The evaluated results are shown in Table 1.

Comparative Example 2

A plurality of solar cell modules were obtained in the same procedure as in Comparative Example 1, except that the thickness of the outermost layer member 505 was changed in 100 µm.

The solar cell modules thus obtained were evaluated in the same procedure in Example 1. The evaluated results are shown in Table 1.

Comparative Example 3

First, there were prepared a back surface insulating layer member 601, a back surface side filler material member 602, a photovoltaic element (solar cell) 603, a glass fiber reinforced member 604, a front surface side filler material member 605, a glass fiber reinforced member 606 and an outermost layer member 607. These members were then laminated as shown in FIG. 6 in the same procedure as in Example 1, to prepare a solar cell module.

The back surface insulating layer member 601, back surface side filler material member 602, photovoltaic element (solar cell) 603, and outermost layer member 607 were made to be the same as those in Example 1. The front surface side filler material member 604 was prepared in the same procedure as in Example 1, except that the thickness was changed in 350 µm. As each of the glass fiber reinforced members 604 and 606, glass fiber unwoven fabric (trademark name: Crane Glass 230, produced by Crane Glass Company) was used. Thus, a plurality of the solar cell modules were obtained.

The solar cell modules thus obtained were evaluated in the same procedure as in Example 1. The evaluated results are shown in Table 1.

As is apparent from Table 1, in the solar cell module of the present invention, even when any external force is applied, the photovoltaic element is stabilized and the surface coating material is excellent in weatherability, heat resistance and moisture resistance, without generation of any separation; and the photovoltaic element is prevented from being deteriorated even upon use in outdoors for a long period of time, thus achieving a desired photoelectric conversion efficiency.

Specifically, the solar cell module of the present invention comprises a photovoltaic element (solar cell) enclosed by a filler material and a coating material having a three-layered structure which is disposed on the light receiving side of the photovoltaic element, wherein said coating element includes a hard resin layer having a hardness of 50 or more in Shore hardness D; an adhesive layer having a function of absorbing ultraviolet rays of such a wavelength to deteriorate said hard resin layer and of transmitting ultraviolet rays necessary for power generation of the photovoltaic element and also having a layer adhesive function; and an outermost layer excellent in weatherability (the resin itself being excellent in a stability against heat, light and moisture), said hard resin layer, adhesive layer and outermost layer being laminated in this order. The inventive solar cell module, therefore, can attain the following effects: (1) to prevent the photovoltaic element from being applied with an external pressure and hence to protect the solar cell; (2) to satisfy weatherability, heat resistance, moisture resistance and scratch resistance necessary for the solar cell module; (3) to ensure the adhesiveness with the photovoltaic element (solar cell); (4) to suppress the deterioration of the photovoltaic element (solar cell) due to moisture permeation at minimum; and (5) to achieve a desired conversion efficiency of the photovoltaic element for a long term of time.

Table 1

	scratch test	Hail impact test	adhesive strength in high temperature/high moisture	weatherability		durability against temperature change
				appearance	conversion efficiency	
Example 1	○	◎	◎	◎	0.99	◎
Example 2	○	◎	◎	◎	0.98	◎
Example 3	○	◎	◎	◎	0.99	◎
Example 4	○	◎	○	◎	0.98	◎
Example 5	○	◎	◎	◎	0.99	○
Comparative Example 1	X	X	○	○	0.95	○
Comparative Example 2	○	X	○	○	0.95	X
Comparative Example 3	○	○	○	○	0.96	○

Claims

1. A solar cell module comprising a photovoltaic element having a semiconductor photoactive layer as a light conversion member, said photovoltaic element being enclosed by a filler material, wherein a hard resin layer, an adhesive layer and an outer layer are laminated on the light receiving surface side of said photovoltaic element in this order.

2. A solar cell module according to claim 1, wherein said hard resin layer is made of a resin having a hardness of 50 or more in Shore hardness D.

3. A solar cell module according to claim 1 or 2, wherein said hard resin layer is one kind selected from polycarbonate resin and polyester resin.

4. A solar cell module according to any of claims 1 to 3, wherein the thickness of said hard resin layer is in the range of from 50 to 125 µm.

5. A solar cell module according to any of claims 1 to 4, wherein said adhesive layer is made of a thermoplastic resin mixed with a ultraviolet absorbent.

6. A solar cell module according to claim 5, wherein said adhesive layer has a total light transmissivity which is 90% or more for light having a wavelength of 400 nm or more; 50% or more for 380 nm, and 10% or less for 350 nm or less.

7. A solar cell module according to claim 5 or 6, wherein the thermoplastic resin of said adhesive layer is one kind selected from ethylene-vinyl acetate copolymer (EVA), polyvinyl butyral (PVB), silicon resin and acrylic resin.

8. A solar cell module according to any of claims 1 to 7, wherein the thickness of said adhesive layer is in the range of from 50 to 200 μm.

9. A solar cell module according to any of claims 1 to 8, wherein said outermost layer is made of a resin having a contact angle against water in the range of 70° or more.

10. A solar cell module according to claim 9, wherein said outermost layer is made of fluororesin.

11. A solar cell module according to any of claims 1 to 10, wherein said semiconductor photoactive layer is an amorphous semiconductor thin film.

12. A solar cell module according to claim 11, wherein said amorphous semiconductor thin film is made of amorphous silicon.

FIG. 1

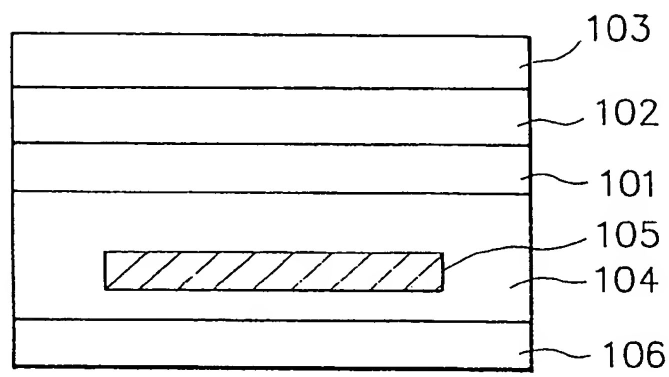


FIG. 2

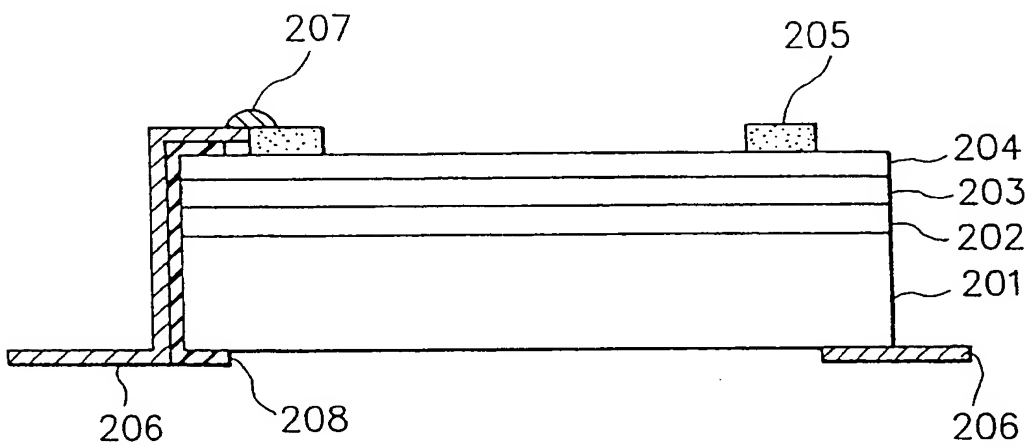


FIG. 3

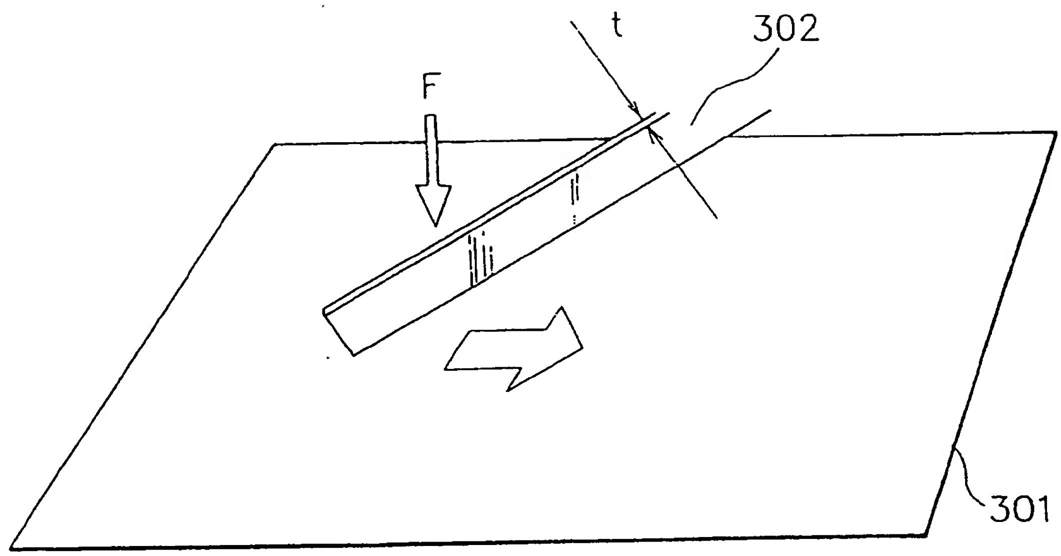


FIG. 4

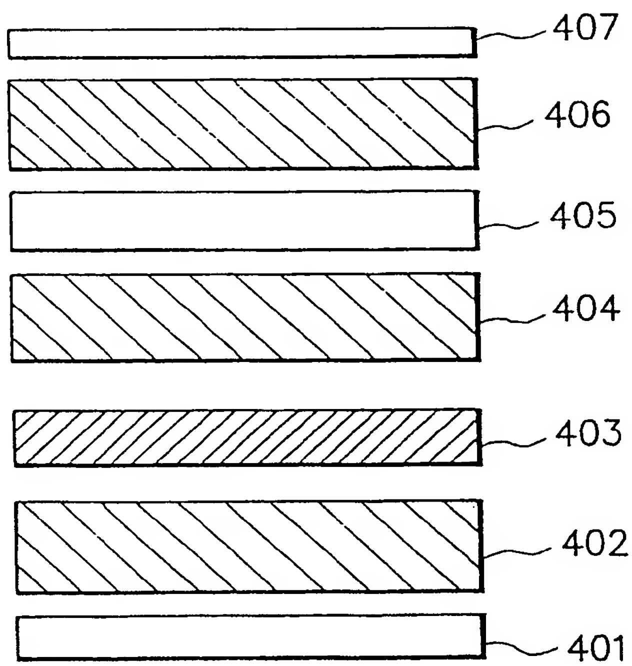


FIG. 5

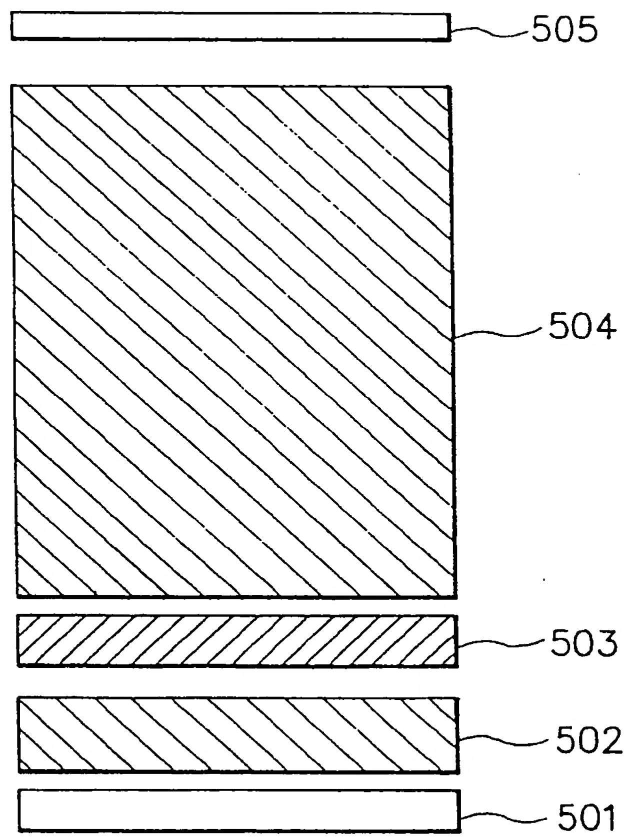
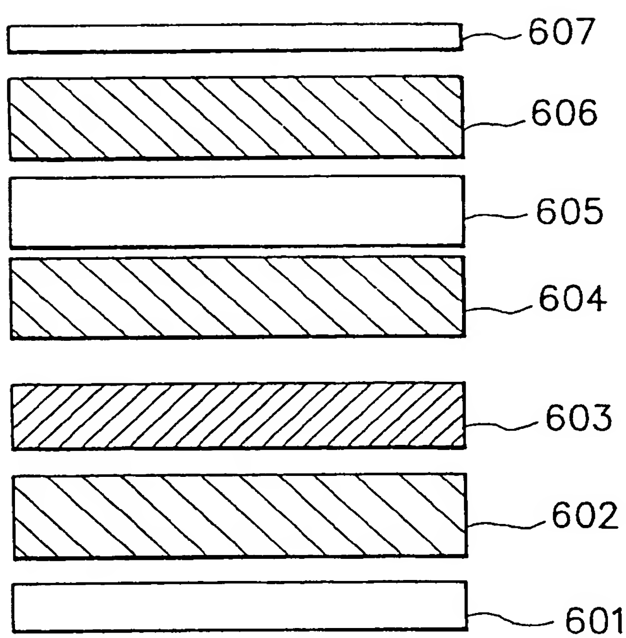


FIG. 6



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP94/01639

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl[6] H01L31/048

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl[5] H01L31/048

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1955 - 1994
Kokai Jitsuyo Shinan Koho 1971 - 1994

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, A, 57-143872 (Nippon Sheet Glass Co., Ltd.), September 6, 1982 (06. 09. 82),	1, 3, 7, 8
Y	Line 15, upper left column to line 3, upper right column, page 3, Fig. 1,	4
A	Lines 3 to 8, upper right column, page 3, lines 10 to 18, lower left column, page 1, line 5, lower right column, page 1 to line 11, upper left column, page 2, lines 9 to 13, lower left column, page 3, lines 8 to 10, page 3, (Family: none)	2, 5, 6, 9-12
Y	JP, A, 61-49482 (Sanyo Electric Co., Ltd.), March 11, 1986 (11. 03. 86) Line 16, upper right column to line 8, lower left column, page 2, Fig. 2, line 7, upper left column, page 3, (Family: none)	1, 7, 8 11, 12
Y	JP, A, 5-235393 (Matsushita Electric Ind. Co., Ltd.),	1, 3, 10 11, 12
A	September 10, 1993 (10. 09. 93) Lines 9 to 11, column 4, lines 2 to 4,	2, 9

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:
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"E" earlier document but published on or after the international filing date
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"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
December 6, 1994 (06. 12. 94)	December 27, 1994 (27. 12. 94)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP94/01639

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	column 4, lines 5 to 6, column 5, Figs. 1, 2, (Family: none)	
Y	Microfilm of the specification and drawings annexed to the written application of Japanese Utility Model Application No. 178186/1981 (Laid-Open No. 83164/1983) (NEC Corp.), June 6, 1983 (06. 06. 83), Fig. 2, (Family: none)	1, 10
Y	JP, A, 57-1263 (Fuji Electric Co., Ltd.), January 6, 1982 (06. 01. 82) Lines 9 to 11, lower left column, page 1, Fig. 3, (Family: none)	5, 11, 12 6
Y A	JP, A, 59-16388 (Matsushita Electric Ind. Co., Ltd.), January 27, 1984 (27. 01. 84) Lines 13 to 17, lower left column, page 1, (Family: none)	5 6